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## MAGNETIC PROPERTIES OF PROTACTINIUM TETRACHLORIDE\*

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## ABSTRACT

Magnetic susceptibility of  $\text{PaCl}_4$  was measured from 3.2 to 296°K with a vibrating-sample magnetometer at fields up to 12 000 Oe.  $\text{PaCl}_4$  has a ferromagnetic transition at  $T_c = 182 \pm 2^\circ\text{K}$ . Below  $T_c$  the magnetization deviates markedly from Brillouin behavior and is far from saturation at 12 kOe; hysteresis is absent above 3.3°K. A high degree of covalency is suggested to explain the high Curie point; a large anisotropy energy is indicated by the lack of saturation. From 180 to 210°K,  $\text{PaCl}_4$  obeys the Curie-Weiss law,  $\chi = C/(T - \theta)$ , with  $\theta = 157^\circ\text{K}$  and  $\mu_{\text{eff}} = 1.04 \mu_B$ . The measured paramagnetic properties were compared to those calculated from crystal-field theory, with and without J-mixing included. The comparison indicates that J-mixing is significant in  $\text{PaCl}_4$ .

## INTRODUCTION

The  $\text{Pa}^{4+}$  ion has the least complicated configuration,  $5f^1$ , of the actinide ions, and is thus an attractive ion for magnetic and optical studies of its crystal-field levels. However, the rarity of protactinium has prevented extensive studies of  $\text{Pa}^{4+}$ . Axe, *et al.*, made paramagnetic resonance and optical studies<sup>1-3</sup> of  $\text{Pa}^{4+}$  in  $\text{Cs}_2\text{ZrCl}_6$ , but no magnetic susceptibility measurements on  $\text{Pa}^{4+}$  compounds have been reported. This paper reports magnetic susceptibility measurements on  $\text{PaCl}_4$  for the temperature range 3.2 to 296°K, and compares the results to the isostructural  $\text{NpCl}_4$  previously studied.<sup>4</sup>

## EXPERIMENTAL

## Sample Preparation

$\text{PaCl}_4$  was prepared by an adaptation of the procedures of Brown and Jones.<sup>5,6</sup>  $\text{K}_2\text{PaF}_7$  was dissolved in hot water, and a mixture of Pa(V) hydrous oxides and oxyfluorides precipitated by adding a KOH solution. These solids were redissolved in 12M HCl-0.1M HF; Pa(V) hydrous oxides, fairly free from oxyfluorides, precipitated with KOH. The Pa(V) hydrous oxides were dried first at 110°C and then at 400°C in vacuum. The dry oxide was reacted with  $\text{SOCl}_2$  vapor in a sealed tube to produce  $\text{PaCl}_5$ , which sublimed free from unreacted solids.  $\text{PaCl}_5$  was reduced to  $\text{PaCl}_4$  with excess aluminum powder at 550°C in a sealed tube; the  $\text{PaCl}_4$  product from this reaction was dark grey from occluded aluminum. Pure  $\text{PaCl}_4$  was obtained by sealing the impure material in a quartz tube, then lowering the tube at 0.02 cm/min through a vertical furnace heated to 800°C. The light yellow  $\text{PaCl}_4$  flowed to the bottom; the aluminum metal and other impurities rose to the top and were easily separated mechanically. The x-ray diffraction pattern of a powdered sample of  $\text{PaCl}_4$  was in exact agreement with the published

diffraction pattern,<sup>6</sup> and, except for minor differences in d values, also identical with the x-ray diffraction pattern of  $\text{UCl}_4$ . The absence of a significant level of impurities was assumed from the absence of extra lines in the x-ray diffraction pattern.

### Measurements

Magnetic susceptibility measurements were made with a vibrating-sample magnetometer<sup>7</sup> which was calibrated with a nickel standard.<sup>8</sup> The magnetic field was continuously variable from 0.1 to 12 kOe and could be reversed. Samples were sealed in plastic containers and cooled in a variable-temperature liquid-helium Dewar. Temperatures were controlled by pumping on the cold helium vapor passing over the sample and by adjusting the current through a resistance heater located below the sample. For the range 3.2 to 70°K, the temperature was measured with a germanium resistance thermometer mounted near the sample; readings were corrected for the field dependence of this thermometer. Between 70 and 296°K, temperatures were measured<sup>9</sup> with two copper-constantan thermocouples, mounted above and below the sample and referenced to liquid-nitrogen.

### RESULTS

Magnetic susceptibility data for  $\text{PaCl}_4$  are summarized in Table I together with previous results<sup>4,10</sup> for  $\text{NpCl}_4$  and  $\text{UCl}_4$ . Both  $\text{PaCl}_4$  and  $\text{NpCl}_4$  have ferromagnetic transitions, but at widely different temperatures. Paramagnetic data can usually be represented by the Curie-Weiss law,

$$\chi = C/(T - \theta) \quad (1)$$

over some regions of temperature T.  $\theta$  is the paramagnetic Curie temperature,

and  $C$  is the Curie constant. In regions where the Curie-Weiss law holds, paramagnetic behavior can be described by an effective moment:

$$\mu_{\text{eff}} = (3kTX/N\mu_B^2)^{1/2} = 2.83 C^{1/2} \quad (2)$$

For states which are twofold degenerate, the average effective  $g$  value,  $g_{\text{av}}$ , is related to the experimental magnetic moment:

$$g_{\text{av}} = \mu_{\text{eff}}/[S'(S'+1)]^{1/2} = (2/\sqrt{3})\mu_{\text{eff}} \quad (3)$$

where  $S'$  is an effective spin of  $1/2$ . Values of  $\mu_{\text{eff}}$ ,  $\theta$ ,  $g_{\text{av}}$ , and the ferromagnetic Curie temperature,  $T_C$ , are given in Table I.

The field dependence of the specific magnetization for  $\text{PaCl}_4$  is shown in Fig. 1 for several temperatures from 167 to 296°K. A slight hysteresis was observed at 3.29°K but not at higher temperatures. Investigations of magnetization as a function of temperature revealed a ferromagnetic transition at approximately 182°K. Temperature dependence of the magnetization at 500 Oe is shown in Fig. 2. The sharp increase in the magnetization at the transition temperature, which is typical of ferromagnets, is clearly evident.

Two methods were employed to locate the Curie temperature of  $\text{PaCl}_4$ , as shown in the insets of Fig. 2. In the region above the transition, lines of constant magnetization were extrapolated to zero applied field to locate the transition temperature at  $182 \pm 2^\circ\text{K}$ . In the region immediately below the Curie temperature, the small-argument expansion of the Brillouin function yields<sup>11</sup>

$$[\sigma(T)/\sigma(0)]^2 = A[1 - (T/T_C)] \quad (4)$$

where  $A$  is a constant, and  $\sigma$  is the specific magnetization. The intercept

at  $\sigma^2 = 0$  gives  $T_c = 181.7^\circ\text{K}$ . There is good agreement between the values of the Curie point determined by the two methods.

At temperatures above  $182^\circ\text{K}$ , the magnetization isotherms display unsaturated paramagnetic behavior. The temperature dependence of the reciprocal susceptibility in this region is shown in Fig. 3. From the Curie temperature to about  $210^\circ\text{K}$ , the data can be represented by the Curie-Weiss law with an effective moment of  $1.04 \mu_B$  and with  $g_{av} = 1.20$ . Above  $210^\circ\text{K}$ , the reciprocal susceptibility deviates markedly from the Curie-Weiss law.

## DISCUSSION

### Ferromagnetic Properties

$\text{PaCl}_4$  and  $\text{NpCl}_4$  are isostructural,<sup>12-14</sup> with  $D_{2d}$  site symmetry for the actinide ion in a tetragonal unit cell. Both are ferromagnetic insulators, but their Curie temperatures,  $182$  and  $6.7^\circ\text{K}$ , respectively, are widely different. The Curie temperatures of  $\text{PaCl}_4$  and some other ferromagnetic insulators are compared in Table II. Because the lattice parameters of  $\text{PaCl}_4$  are slightly larger than those of  $\text{NpCl}_4$ , the Curie point of  $\text{PaCl}_4$  was expected to be lower than that of  $\text{NpCl}_4$ . However, because the Curie point of  $\text{PaCl}_4$  is considerably higher than that of  $\text{NpCl}_4$ , factors other than the geometric arrangement of atoms in the crystal must also be important for the magnetic ordering phenomenon in  $\text{PaCl}_4$ .

In Fig. 2, the experimental magnetization is compared with theoretical Brillouin curves, including the applied field, for several values of  $J$ . Although the experimental magnetization resembles the Brillouin curves, the quantitative agreement is poor immediately below the transition temperature.

Similar disagreement<sup>4</sup> was found in the case of  $\text{NpCl}_4$ . Short-range ordering is indicated by a finite value of the magnetization above the transition temperature.

Ferromagnetic  $\text{PaCl}_4$  does not saturate in the largest fields employed, suggesting a large anisotropy energy.<sup>15</sup> Compared with  $\text{NpCl}_4$ , which does not show this large anisotropy energy,<sup>4</sup> the protactinium atom in  $\text{PaCl}_4$  has a larger interaction with its environment. This interaction, together with the higher Curie temperature of  $\text{PaCl}_4$  is consistent with the hypothesis that a greater degree of covalency in  $\text{Pa}^{4+}$  ( $5f^1$ ) than in  $\text{Np}^{4+}$  ( $5f^3$ ) provides a more effective path for cooperative magnetic phenomena.

Spectral evidence indicates greater covalency for the  $5f^1$  configuration than for other  $5f^n$  configurations. For example, the  $\text{U}^{5+}$  ion, isoelectronic with  $\text{Pa}^{4+}$ , has crystal-field parameters<sup>16</sup> of 2429 and  $6739 \text{ cm}^{-1}$  in  $\text{CsUF}_6$ ; these change markedly<sup>17</sup> to 1920 and  $4580 \text{ cm}^{-1}$  for  $\text{U}^{5+}$  in  $\text{UCl}_5 \cdot \text{SOCl}_2$ . Presuming that the sensitivity of the energy levels to environment is a property of all ions of the  $5f^1$  configuration, the  $\text{Pa}^{4+}$  ion might also be expected to have a strong ion-ligand interaction.

For the  $5f^2$  configuration of  $\text{U}^{4+}$ , however, Slater integrals and spin-orbit coupling constants have been found to be essentially unchanged<sup>18-19</sup> for the different host lattices  $\text{ZrSiO}_4$ ,  $\text{Cs}_2\text{ZrCl}_6$ , and  $[(\text{CH}_3)_4\text{N}]_2\text{UBr}_6$ . The lack of variation in these parameters for  $5f^2$  in the different hosts implies that covalent contributions are equal and probably small, as the electronegativities of oxide, chloride, and bromide ions are substantially different. The low degree of covalency in the  $\text{U}^{4+}$  ion-ligand interaction suggests a contraction of the f orbitals in the  $5f^2$  configuration relative to the f orbitals in the  $5f^1$  configuration. The f orbitals for  $5f^3$  ( $\text{Np}^{4+}$ ) would be expected to interact



to a lesser degree than  $5f^2$ , and have comparatively low covalent character. Other factors may also contribute to the wide difference in Curie temperatures between  $\text{PaCl}_4$  and  $\text{NpCl}_4$ , but differences in covalent contributions appear to be paramount.

The large intermetallic distance between  $\text{Pa}^{4+}$  ions precludes direct exchange interaction. The Bloembergen-Rowland interaction which has been postulated to explain the ferromagnetic behavior<sup>20</sup> of the insulator  $\text{EuO}$  is probably not the responsible mechanism, because the relative importance of such an interaction decreases with increasing covalency; the less covalent compound  $\text{NpCl}_4$  would have the higher transition temperature by this mechanism. The magnetic ordering of  $\text{PaCl}_4$  almost certainly results from the indirect exchange through bridging chloride ions.

The paramagnetic Curie temperature  $\theta$  of  $\text{PaCl}_4$  is lower than  $T_c$ , which is common for antiferromagnets, but not for ferromagnets.<sup>21</sup> A possible explanation is that excited crystal-field levels begin to be populated at temperatures near the Curie point; in that case, the simple Curie-Weiss treatment would not be applicable. There is not yet sufficient evidence to explain the anomalously low value of  $\theta$ .

### Paramagnetic Properties

The measured magnetic moment of the lowest crystal-field level of a compound is directly related to the wave function of that level, which in turn is related to splittings produced by the crystal field. Although the parameters describing the crystal field are usually too numerous to be determined by the magnetic moment alone, the moment in combination with other data can provide useful information on the nature of the ground-state wave function. In the case of  $\text{Pa}^{4+}$ , the  $5f^1$  configuration contains only one term,

$^2F$ , which is split into two levels,  $J = 5/2$  and  $J = 7/2$ , by the spin-orbit interaction. The  $^2F_{5/2}$  ground state is separated from the  $^2F_{7/2}$  state by about  $5215 \text{ cm}^{-1}$ ; the  $J$  levels are further split by the crystal field, although by Kramers' theorem each crystal-field level is at least two-fold degenerate. In  $\text{PaCl}_4$ , each  $\text{Pa}^{4+}$  ion is at the center of a distorted tetrahedron of  $\text{Cl}^-$  ions, with  $D_{2d}$  site symmetry.<sup>12-14</sup> The crystal-field Hamiltonian contains the potential  $V$  which may be expanded in terms of tensor operators  $C_q^{(k)}$ ; for  $D_{2d}$  symmetry, the potential is<sup>22</sup>

$$V = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_4^4 (C_{-4}^{(4)} + C_4^{(4)}) + B_0^6 C_0^{(6)} + B_4^6 (C_{-4}^{(6)} + C_4^{(6)}) \quad (5)$$

where  $B_q^k$  are the crystal-field parameters (unknown for  $\text{PaCl}_4$ ).

In  $D_{2d}$  symmetry, a state with  $J = 5/2$  splits into three Kramers doublets; using  $|J, \pm J_z\rangle$  basis functions, the wave functions of the crystal-field levels are

$$\psi_a = |5/2, \pm 1/2\rangle \quad (6a)$$

$$\psi_b = \pm \cos\alpha |5/2, \pm 5/2\rangle \pm \sin\alpha |5/2, \mp 3/2\rangle \quad (6b)$$

$$\psi_c = \pm \cos\beta |5/2, \pm 5/2\rangle \pm \sin\beta |5/2, \mp 3/2\rangle \quad (6c)$$

where the mixing parameters  $\alpha$  and  $\beta$  depend on the crystal-field parameters. Using wave functions of this form and designating the components of a Kramers doublet as  $|+\rangle$  and  $|-\rangle$ , magnetic properties of a level may be calculated from<sup>23</sup>

$$g_{||} = 2 |\langle + | L_z + 2S_z | + \rangle| \quad (7a)$$

$$g_{\perp} = 2 |\langle + | L_x + 2S_x | - \rangle| \quad (7b)$$

$$g_{av} = [(g_{||}^2 + 2g_{\perp}^2)/3]^{1/2} \quad (7c)$$

For the wave functions of Eq. (6),  $g_{av}$  may be calculated as a function of  $\alpha$  (or  $\beta$ ), as shown in Fig. 4.

The apparent Curie-Weiss behavior of  $\text{PaCl}_4$  between 182 and 210°K suggests that the lowest crystal-field level is reasonably well isolated, with an experimental  $g_{av} = 1.20$ . This value is unexpectedly small, because the wave functions of Eq. (6) yield a calculated  $g_{av} > 1.20$  for all values of the mixing parameter. The experimental and calculated values of  $g_{av}$  are compared in Fig. 4. Thus, the crystal-field wave functions of a pure state with  $J = 5/2$  are inadequate to describe the detailed magnetic properties of  $\text{PaCl}_4$ ; however, wave functions with the form of Eq. (6) are useful as first approximations.

Although the crystal-field parameters of  $\text{PaCl}_4$  are unknown, those of isostructural  $\text{UCl}_4$  have been determined by optical spectroscopy.<sup>24</sup> The  $\text{UCl}_4$  parameters were used in crystal-field calculations on  $\text{PaCl}_4$  to obtain approximate eigenvalues and eigenfunctions, assuming the parameters of  $\text{UCl}_4$  and  $\text{PaCl}_4$  are not greatly different. Crystal-field matrix elements of Eq. (5) were calculated by the tensor operator method of Wybourne,<sup>22</sup> with corrected definitions<sup>25</sup> of  $B_q^k$ . Diagonalization of the crystal-field matrix for the pure state with  $J = 5/2$  (no J-mixing) gave the following wave function for the lowest level:

$$|\pm\rangle = \pm 0.459|5/2, \pm 5/2\rangle \pm 0.888|5/2, \mp 3/2\rangle$$

Applying Eq. (7) to this wave function yields  $g_{av} = 1.43$ , about 20% larger than the experimental  $g_{av}$ . Similar difficulties occurred in  $\text{NpCl}_4$  calculations without J-mixing.<sup>4</sup> The crystal-field splittings of the  $^2F$  term of  $\text{Pa}^{4+}$ , from this approximation, are shown in Fig. 5a.

The  $5f^1$  configuration is sufficiently simple that a complete calculation including J-mixing is feasible. The Hamiltonian matrices for the crystal-field and spin-orbit interactions were diagonalized simultaneously, with  $1490 \text{ cm}^{-1}$  as

the spin-orbit coupling parameter.<sup>3</sup> The results of a calculation including J-mixing, but with the same approximate crystal-field parameters as before, gave the energy-level diagram of Fig. 5b. The wave function found for the lowest Kramers doublet was

$$|\pm\rangle = \pm 0.399|5/2, \pm 5/2\rangle \pm 0.843|5/2, \mp 3/2\rangle - 0.310|7/2, \pm 5/2\rangle - 0.187|7/2, \mp 3/2\rangle$$

Calculation of the g tensor for this level from Eq. (7) is straightforward,<sup>23,26</sup> and gives  $g_{av} = 1.24$ , in good agreement with the observed value.

Even though this model successfully reproduces  $g_{av}$  for the lowest crystal-field level, it does not give the correct splitting between the ground and first-excited crystal-field levels. The deviation from Curie-Weiss behavior shown in Fig. 3 indicates that the first-excited crystal-field level is in the range 100 to 300  $\text{cm}^{-1}$ , whereas this calculation predicts 877  $\text{cm}^{-1}$ . Additional calculations, including J-mixing, in which the crystal-field parameters were varied by  $\pm 10\%$  did not change the crystal-field splittings and values of the ground-state  $g_{av}$  appreciably. The lack of accurate crystal-field parameters for  $\text{PaCl}_4$  appears to be the major difficulty with these calculations. However, the calculations indicate that J-mixing in  $\text{PaCl}_4$  must be taken into account to describe properly the paramagnetic properties of the compound.

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## FOOTNOTES

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TABLE I. Magnetic data for some tetravalent actinide chlorides.

Compound	Ground-State Configuration	T <sup>a</sup> (°K)	C <sup>b</sup> (emu-deg-mole <sup>-1</sup> )	θ <sup>b</sup> (°K)	μ <sub>eff</sub> (μ <sub>B</sub> )	g <sub>av</sub> <sup>c</sup>	T <sub>C</sub> <sup>d</sup> (°K)
PaCl <sub>4</sub>	5f <sup>1</sup> 2F <sub>5/2</sub>	182-210	0.13	+158	1.04 ± 0.06	1.20 ± 0.07	182 ± 2
UCl <sub>4</sub> <sup>e</sup>	5f <sup>2</sup> 3H <sub>4</sub>	90-551	1.35	- 65	3.29	3.79	-
NpCl <sub>4</sub> <sup>f</sup>	5f <sup>3</sup> 4I <sub>9/2</sub>	7-43	1.19	+6.9	3.08	3.55	6.7 ± 0.1

<sup>a</sup> Region exhibiting Curie-Weiss behavior.

<sup>b</sup> Paramagnetic constants from Curie-Weiss law  $\chi = C/(T - \theta)$ .

<sup>c</sup>  $g_{av} = [(g_{||}^2 + 2g_{\perp}^2)/3]^{1/2}$ ;  $g_{||} = 2|\langle +|L_z + 2S_z|+ \rangle|$ ;  $g_{\perp} = 2|\langle +|L_x + 2S_x|- \rangle|$ .

<sup>d</sup> Ferromagnetic transition temperature.

<sup>e</sup> From Reference 10.

<sup>f</sup> From Reference 4.

TABLE II. Ferromagnetic transition temperatures of some rare earth and actinide halides.

Compound	$T_c$ ( $^{\circ}\text{K}$ )	Reference
$\text{CeCl}_3$	0.345	27
$\text{NdCl}_3$	1.745	27
$\text{GdCl}_3$	2.2	28
$\text{EuI}_2$	5	29
$\text{NpCl}_4$	6.7	4
$\text{PaCl}_4$	182	This work



## FIGURE CAPTIONS

Fig. 1. Magnetization isotherms of a powdered sample of  $\text{PaCl}_4$ .

Fig. 2. Specific magnetization versus temperature at 500 Oe, showing a ferromagnetic transition in  $\text{PaCl}_4$ . Brillouin curves (including an applied field of 500 Oe) are shown:  $J = 3/2$  (dashed curve),  $J = 5/2$  (solid curve),  $J = 7/2$  (broken curve). The determination of the Curie point, by two different methods is illustrated in insets A and B.

Fig. 3. Reciprocal susceptibility of  $\text{PaCl}_4$  as a function of temperature. The Curie-Weiss region has a magnetic moment of  $1.04 \mu_B$  (solid line). Deviation from Curie-Weiss behavior above  $210^\circ\text{K}$  is indicated by the broken line.

Fig. 4. Theoretical  $g_{av}$  for crystal-field levels of a pure state with  $J = 5/2$ , in  $D_{2d}$  symmetry. The experimental  $g_{av}$  is shown for comparison. (A) For  $\psi = \pm \cos\alpha |5/2, \pm 5/2\rangle \pm \sin\alpha |5/2, \mp 3/2\rangle$ . (B) For  $\psi = |5/2, \pm 1/2\rangle$ .

Fig. 5. Crystal-field splittings of the  $^2F$  term of  $\text{Pa}^{4+}$ , with and without J-mixing. The crystal-field parameters of  $\text{PaCl}_4$  were approximated by those of  $\text{UCl}_4$ .

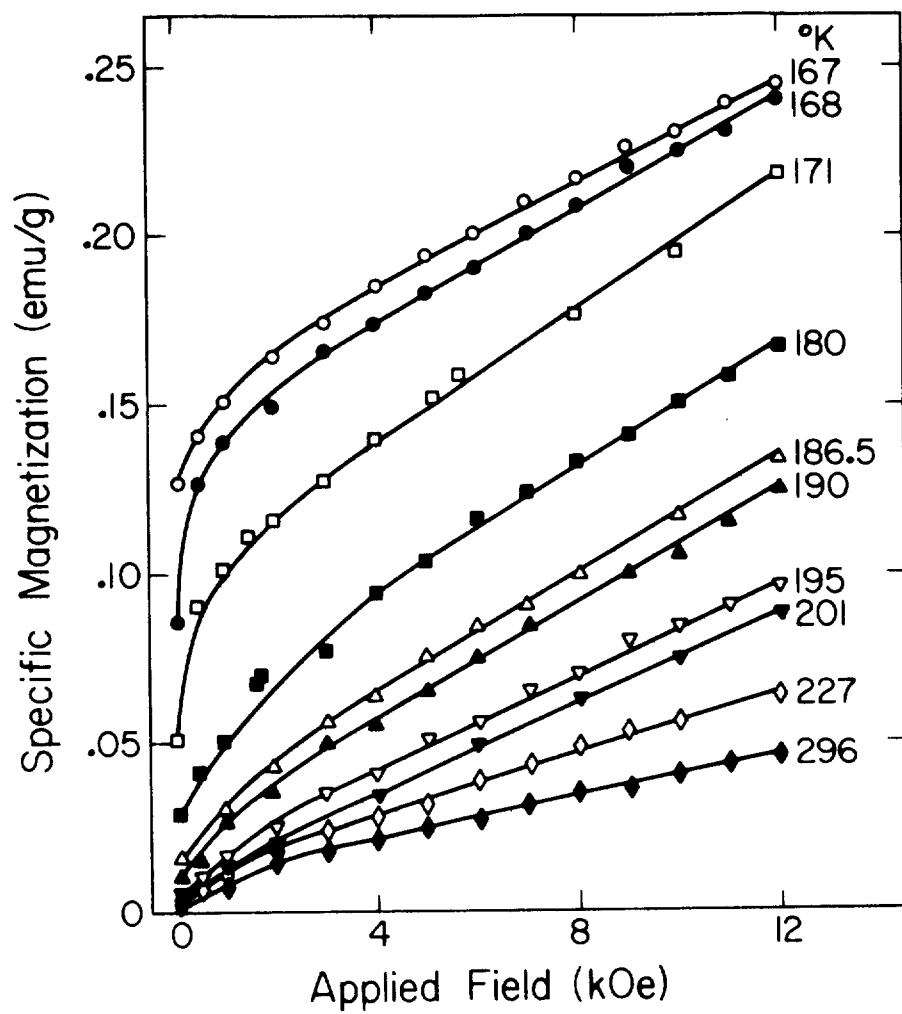


Fig. 1. Magnetization isotherms of a powdered sample of  $\text{PaCl}_4$ .

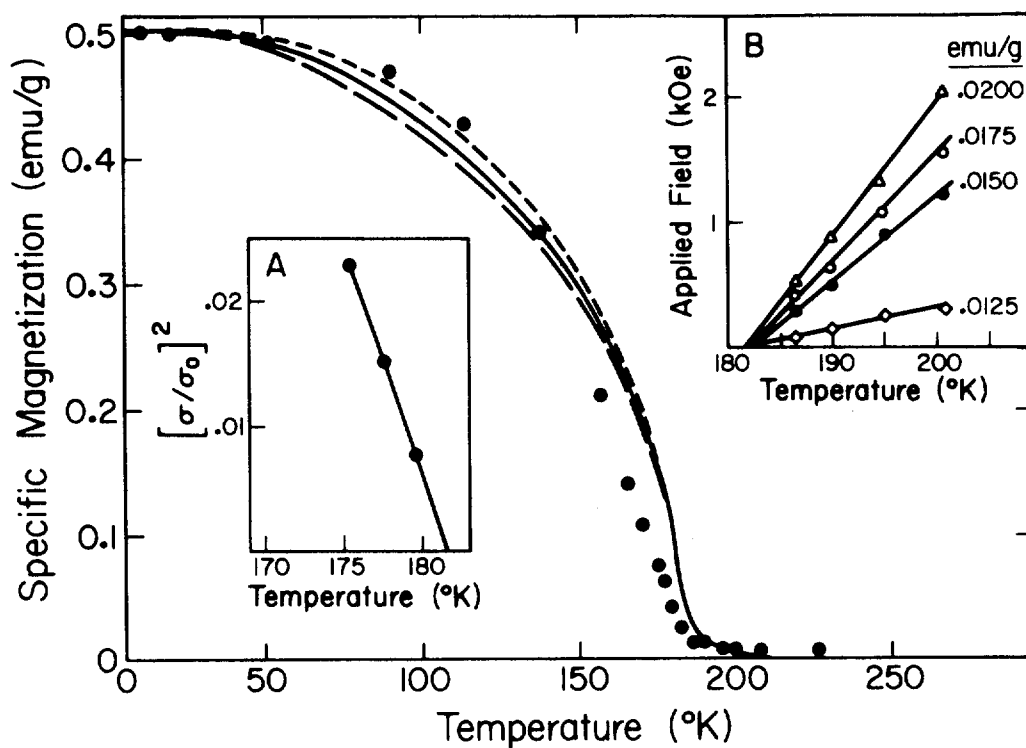


Fig. 2. Specific magnetization versus temperature at 500 Oe, showing a ferromagnetic transition in  $\text{PaCl}_4$ . Brillouin curves (including an applied field of 500 Oe) are shown:  $J = 3/2$  (dashed curve),  $J = 5/2$  (solid curve),  $J = 7/2$  (broken curve). The determination of the Curie point by two different methods is illustrated in insets A and B.

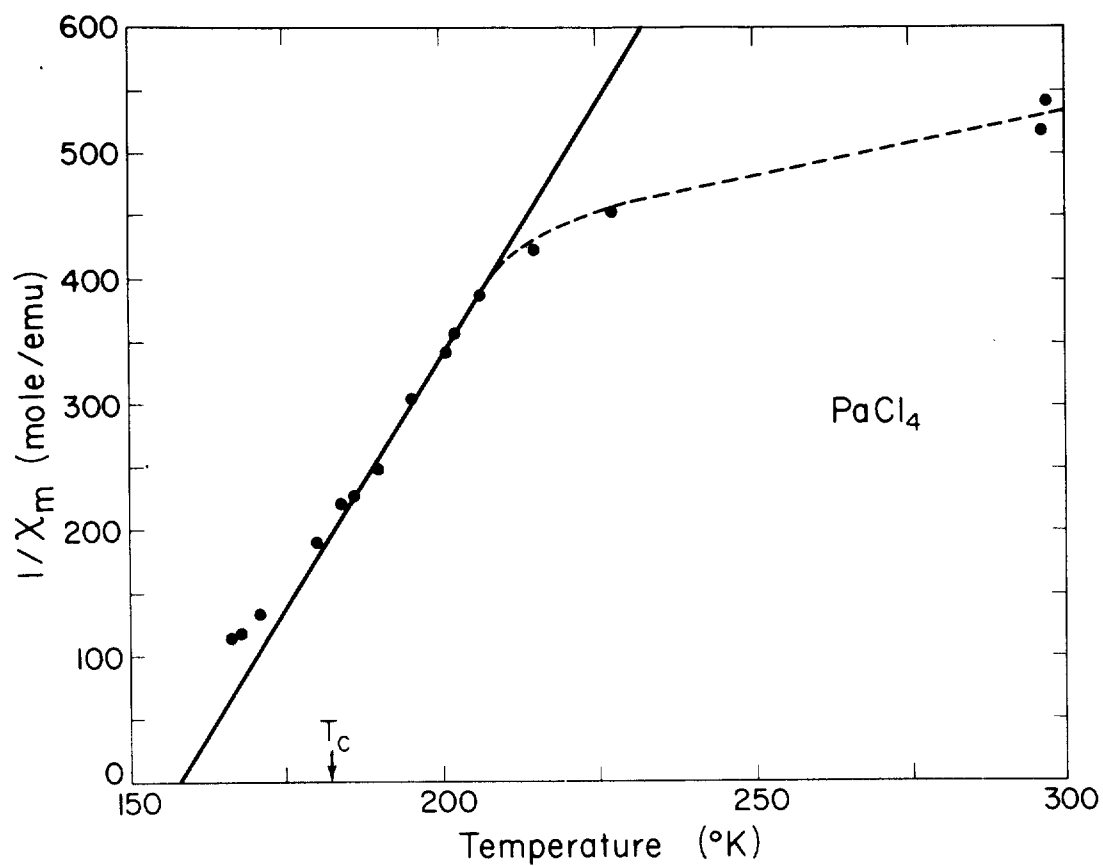


Fig. 3. Reciprocal susceptibility of  $\text{PaCl}_4$  as a function of temperature. The Curie-Weiss region has a magnetic moment of  $1.04 \mu_B$  (solid line). Deviation from Curie-Weiss behavior above  $210^\circ\text{K}$  is indicated by the broken line.

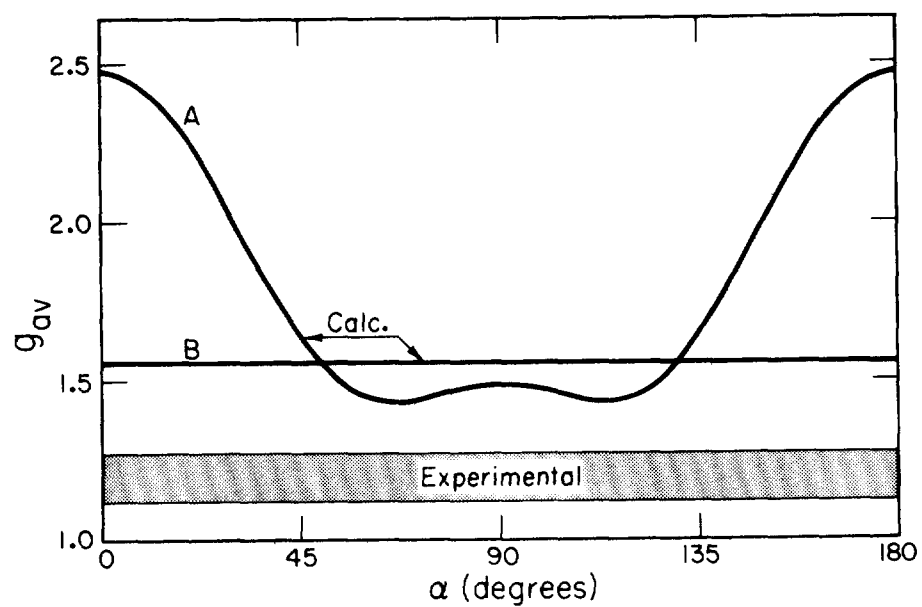


Fig. 4. Theoretical  $g_{av}$  for crystal-field levels of a pure state with  $J = 5/2$ , in  $D_{2d}$  symmetry. The experimental  $g_{av}$  is shown for comparison. (A) For  $\psi = \pm \cos \alpha |5/2, \pm 5/2\rangle \pm \sin \alpha |5/2, \mp 3/2\rangle$ . (B) For  $\psi = |5/2, \pm 1/2\rangle$ .

A. Without J-Mixing

B. With J-Mixing

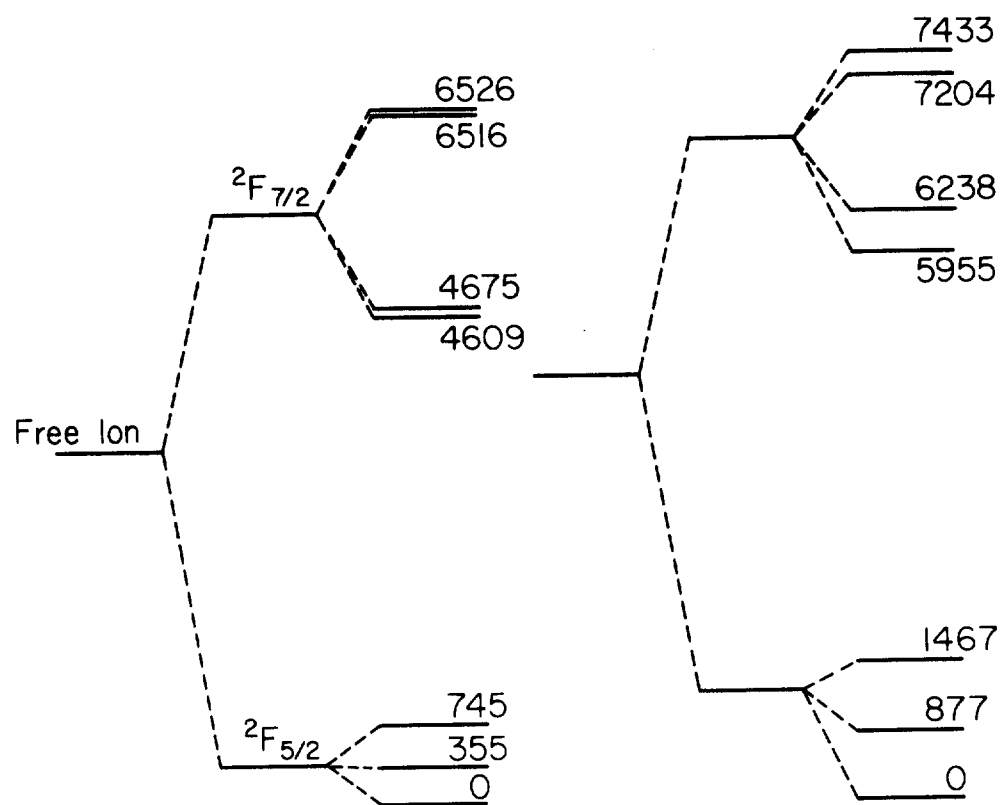


Fig. 5. Crystal-field splittings of the  $^2F$  term of  $\text{Pa}^{4+}$ , with and without J-mixing. The crystal-field parameters of  $\text{PaCl}_4$  were approximated by those of  $\text{UCl}_4$ .